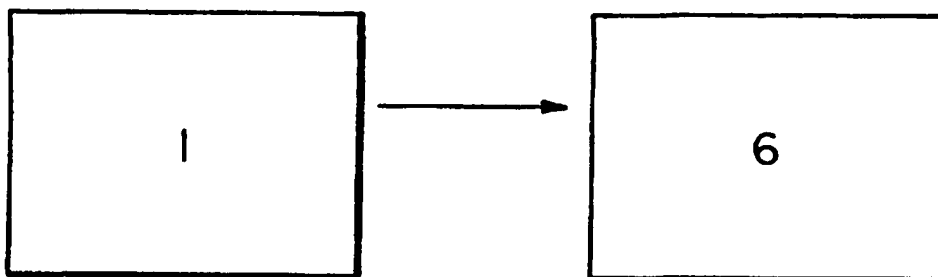




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(54) Title: PROCESS FOR FORMING ARTICLES DIRECTLY FROM MELT POLYMERIZATION



(57) Abstract

The present invention provides a process comprising the steps of a) melt reacting at least one glycol and at least one dicarboxylic acid to form a polyester having an IhV of at least about 0.5 dl/g, wherein said at least one glycol is selected from the group consisting of glycols having up to 10 carbon atoms and mixtures thereof and said dicarboxylic is selected from the group consisting of alkyl dicarboxylic acids having 2 to 16 carbon atoms, aryl dicarboxylic acids having 8 to 16 carbon atoms and mixtures thereof; and b) forming said polyester into shaped articles directly from step a). Thus, the present invention provides a direct melt to mold process for forming polyester articles.

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PROCESS FOR FORMING ARTICLES DIRECTLY FROM
MELT POLYMERIZATION

Background of the Invention

5 Polyesters are widely used in the manufacture of
fibers, molded objects, films, sheeting, food trays, as
well as food and beverage containers. These polymers
are generally made by batch or continuous melt phase
polycondensation reactions well known in the art. The
10 polymers are then pelletized and used in various
extrusion or molding operations. In certain
applications where high molecular weight polymers are
required, the pellets are subjected to "solid state"
polycondensation conditions in which the inherent
15 viscosity (IhV) value is significantly increased. Such
solid state polycondensation reactions are required
since the melt viscosity of polyester polymers is quite
high for polymers having IhV values greater than 0.6.

 During the preparation or processing of polyesters
20 in the melt phase, certain byproducts are formed. One
such byproduct is acetaldehyde, and its presence in
molded objects such as food containers, beverage
bottles, water bottles, and the like is quite
deleterious from a taste standpoint. Particularly for
25 sensitive beverages such as cola and water, it is highly
desirable to produce preforms having less than 10 ppm
and preferably less than 5 ppm of acetaldehyde.
Achieving this low level of acetaldehyde is difficult,
however, because, as is well known to practitioners of
30 the art, acetaldehyde is continually formed as a
byproduct during the polymerization and subsequent melt
processing of PET and similar polymers.

 Before the discovery of the present invention,
therefore, a three-stage process has been universally
35 used to provide polyester polymers suitable for uses in

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which it is important to minimize the presence of acetaldehyde. Such a process typically involves the preparation of a relatively low molecular weight precursor polymer, having an IhV value of 0.6, by melt-
5 phase polymerization techniques that are well known in the art. The acetaldehyde content of such a precursor may range from 30 ppm to over 150 ppm, depending on the reaction conditions chosen. This precursor is then cooled, shaped into pellets, crystallized, and subjected
10 to solid-state polymerization. Typically, an inert gas is used to strip glycols, acetaldehyde, and other reaction byproducts from the pellets so that at the end of the solid-state process, the IhV value has been increased to 0.70 or more, and the acetaldehyde content
15 has been reduced to below 1 ppm or less. The product so prepared must still be heated and melted in a third step in order to be formed into a useful shape, such as a beverage bottle preform, and this process typically causes an increase in acetaldehyde content of from less
20 than 1 ppm in the pellets, to up to 8 or 10 ppm or more in the shaped article. This dramatic increase in acetaldehyde occurs despite the fact that the molding process takes typically less than one or two minutes to complete. We have now discovered a process whereby
25 polyesters such as PET and similar polymers may be prepared in the melt, purified of excess acetaldehyde and other byproducts, and molded directly from the melt into useful shaped articles, such as for example beverage bottle preforms, said shaped articles having
30 surprisingly low acetaldehyde content. Not only does the process of the present invention avoid all of the costly additional steps of the conventional process, such as cooling, chopping, drying, crystallizing, solid-state polymerization, and remelting, but the shaped
35 articles produced by our process possess in addition to

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low acetaldehyde content, other superior properties such as for example better color, less loss of molecular weight due to breakdown, and freedom from defects known as "bubbles" and "unmelts" which are sometimes formed during the conventional crystallizing/solid stating and/or molding processes. These and other advantages of the present invention will become apparent in the description which follows.

U.S. Serial No. 08/498,404 describes an apparatus and method for distributing molten polymer to multiple molding machines.

U.S. Serial No. 08/501,114 describes an improved process for lowering the acetaldehyde content of molten PET to levels suitable for direct use in providing articles for food packaging by using an inert gas purge to contact the molten polyester.

Japan Patent Application 53-71162 (1978) describes remelting polyester chips and holding the molten polymer under vacuum to reduce the concentration of acetaldehyde.

U.S. 4,263,425 describes the solid stating of PET pellets to provide polymer having a low concentration of acetaldehyde. The reference discloses partial acetaldehyde elimination via treatment of the stirred melt at higher temperatures under vacuum.

U.S. 4,064,112 describes a method for overcoming sticking problems during the solid stating process. It discloses that melt phase processes without solid stating yield elevated concentrations of acetaldehyde in the melt polyester.

U.S. 4,154,920 describes melt phase polymerization to provide polymer with $IhV = 0.4 - 0.6$ and then solid stating to an IhV greater than 0.7. It also describes the use of thin films to accomplish rapid polymerization such as in a Luwa thin-film evaporator.

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U.S. 4,372,910 describes a method and apparatus for molding hollow plastic articles. It describes remelting pellets in an extruder and extruding hot plasticized resin to sequentially mold preforms from a continuous
5 molten stream and then to directly transfer preforms to a blowing process.

U.S. 4,836,767 describes a method to reduce acetaldehyde during molding. It states that acetaldehyde increases linearly with time and
10 exponentially with temperature.

Japan Patent Application 57-191320 (1982) describes the removal of acetaldehyde from PET polymer to a concentration of less than 300 ppm just prior to melt spinning of fibers.

15 Japan Patent Application 55-069618 (1980) states that PET with acetaldehyde content less than 20 ppm is obtained by melt polymerization followed by extrusion into fiber or film and subsequently passing the fiber or film through a fluid or vacuum. Fluids used included
20 air, nitrogen, water, and steam.

U.S. 5,270,444 and U.S. 5,241,046 describe the treatment of PET with water to reduce the amount of acetaldehyde and cyclic oligomer in the polymer.

U.S. 5,262,513 states that the oligomer content is
25 1-2% in melt phase polymer and 0.5-1.0% in solid stated PET polymer.

U.S. 5,169,582 describes a process in which vacuum is applied to linked, vented extruders to remove monomer from nylon-6 (caprolactam) polymers. U.S. 3,183,366 and
30 3,578,640 disclose the direct spinning of nylon-6.

U.S. 3,657,195 discloses the production of high molecular weight nylon-6,6 by continuous condensation of low molecular weight nylon-6,6 in a vented screw extruder in the presence of steam.

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The following patents disclose various aspects of solid stating: U.S. 4,963,644, 4,223,128, 4,591,629, 4,395,222, 4,374,97 and 5,119,170 and U.S. 5,090,134, which disclose the necessity of solid stating PET polymers to obtain low acetaldehyde concentrations.

U.S. 4,820,795 states that a vessel is prepared by melting the polyester and injecting the melt into a mold. Acetaldehyde concentration is reduced by a combination of catalyst selection and crystallization of the polymer.

U.S. 5,246,992 provides background on the mechanism for acetaldehyde formation from PET and states that thermal decomposition of the PET is influenced by the level of the reaction temperature, the residence time, and possibly by the nature of the polycondensation catalyst.

U.S. 4,237,261 describes the direct spinning process for PET fibers. Such polymers have to have an IhV of only 0.6 and no mention is made of molding articles, minimization of degradation products, or acetaldehyde formation.

U.S. 4,230,819 describes the removal of acetaldehyde from crystalline PET with a dry inert gas (air or nitrogen at 170-250°C). It states that acetaldehyde can not be completely removed from PET by heating it under reduced pressure.

U.S. 4,142,040 states that gaseous oxygen is excluded before melting and during melt processing of PET in order to reduce acetaldehyde formation.

The following patents are concerned with devolatilization of PET:

U.S. 5,102,594 (supplying a thermoplastic condensation polymer in powder form to a vented extruder for devolatilization and melting), U.S. 4,980,105 (devolatilization of polycarbonates in an extruder to

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remove volatiles (especially cyclic dimer) and forcing the melt through a die), U.S. 4,362,852

(devolatilization of molten polymers such as nylon and PET with a rotary disk processor), U.S. 3,486,864

5 (polymerization reactor in which a solid prepolymer is melted and then a vacuum is used to remove volatile glycol products as fast as possible); U.S. 3,913,796 (vent-type injection molding machine in which gases such as moisture, air, and other volatiles can be effectively
10 removed); and U.S. 4,060,226 (vented injection molding screw extruder, with means to vent gases and vapors from the screw barrel, to produce devolatilized plasticized materials such as nylon and other degradable materials).

15 Description of the Drawings

FIGURE 1 is a flow diagram of the present invention.

FIGURE 2 is a flow diagram of the prior art process.

20

Description of the Invention

The present invention provides a process for producing molded articles comprising the steps of:

- 25 a) melt reacting at least one glycol and at least one dicarboxylic acid to form a polyester having an I_{hV} of at least 0.5 dl/g, wherein said at least one glycol is selected from the group consisting of glycols having up to 10 carbon atoms and mixtures thereof and said
30 dicarboxylic is selected from the group consisting of alkyl dicarboxylic acids having 2 to 16 carbon atoms, aryl dicarboxylic acids having 8 to 16 carbon atoms and mixtures thereof; and

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- b) forming said polyester into shaped articles directly from step a.

The term "IhV" used herein refers to the Inherent Viscosity of the polymer, as determined by standard
5 methods on a solution of 0.5 g of polymer dissolved in 100 ml of a mixture of phenol (60% by volume) and tetrachloroethane (40% by volume).

Specifically, the process of the present invention provides a "melt-to-mold" process in which polyester
10 polymers or copolymers are prepared in the melt phase to an IhV value of greater than 0.5 dl/g and then the melt is fed directly from the polycondensation reactor, 1, to at least one molding or shaping machine, 6. Any conventional melt polymerization process capable of
15 producing the required IhV may be used for the polycondensation and the reactor may comprise one or more reaction vessels or zones which are capable of producing polyester having the required IhV. Generally the molten polyester is directed from 1 to 6 by means of
20 a viscous fluid pump, such as an extruder, gear pump or diskpac pump. It should be understood that although only one molding machine is shown in Figure 1, a plurality of molding machines may be used.

Preferably the polymer is devolatilized to remove
25 acetaldehyde and other undesirable volatiles. The devolatilization step may be conducted in a separate devolatilization unit (not shown), concurrently in the polycondensation reactor 1, or concurrently in molding machine, 6.

30 Figure 2 depicts the process practiced prior to the present invention. Common units are numbered as in Figure 1. As in Figure 1, the conventional process begins by forming polymer in a melt polymerization reactor, 1. The molted polymer is directed to a
35 pelletizer (2) where the polymer is extruded into solid

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pellets. After pelletization the pellets may be stored or fed directly to a crystallization unit, 3. After crystallization, the pellets are directed to a solid stating unit, 4, where the Ih.V. and molecular weight of the pellets are increased to the desired level and acetaldehyde is removed. In some processes the crystallization and solid stating units are combined. After solid stating the pellets are stored (either in silos or railcars, 5), shipped to a molder (via railcar), optionally stored again (railcars or silos) and dried. Finally the molder introduces the pellets into an extruder or other molding/shaping device, 6 and makes the final product. Pelletizers, crystallization units, solid stating units, dryers, extruders and molding/shaping devices are all generally known in the art.

Thus, it is clear from comparison of Figures 1 and 2, the process of the present invention eliminates the need for pelletization, crystallization, solid stating, drying, and remelting of the polymer before the molding/shaping device. The elimination of these steps not only results in enormous cost savings (because of the reduced equipment and energy requirements) but also produces polymer which is lower in undesirable contaminants such as acetaldehyde and other volatiles.

The molding shaping device 6 may be any of those generally known in the art. For example, injection molds may be used to form preforms used to blow bottles, food/beverage containers, trays, or other desirable shapes. Also the polymer melts may be used in extrusion blow molding operations to provide bottles, food containers, and the like. The polymer melt may similarly be fed to an extruder to produce films, sheet, profiles, pipe and the like.

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In cases where low acetaldehyde levels are desirable in the final molded object, it has been found that acetaldehyde can be readily removed from the molten polymer using a viscous fluid processor such as an extruder, thin film evaporator, or discpack purged with an inert gas or by subjecting the melt to conditions of vacuum (U.S. Serial No. 08/501,114). Any viscous fluid processor capable of generating a large amount of surface area per unit volume and/or for rapidly regenerating the exposed melt surface can be used for this step. In this manner, acetaldehyde levels can be readily reduced to less than 10 ppm. Typical acetaldehyde levels in polymer coming from the final reactor before this treatment are generally in the range of 30 to over 150 ppm.

After removal of the acetaldehyde, it is important to limit the amount of time the polymer is held in the melt prior to the molding operation because additional acetaldehyde can be generated in molten polymer. Experience with the conventional molding process has shown that the rate at which this additional acetaldehyde accumulates is extremely rapid. For example, the free acetaldehyde content of the polymer may increase from less than 1 ppm in the pellets to over 8 to 10 ppm in the bottle preform, during the less than 1 or 2 minute processing time of a typical molding machine. Such a rapid rate of acetaldehyde buildup would seem to preclude any practical means of distributing and molding continuously-produced molten polymer, no matter how well acetaldehyde could be removed.

However, it was surprising to find that the rate of regeneration of acetaldehyde in our melt to mold process is significantly lower than in polyester melts provided by remelting pellets. Thus, molten polymer produced by

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our method may be held in the melt during processing for a substantially longer time without undue acetaldehyde buildup. Nevertheless, in our melt to mold process, it is desirable to limit the amount of time in the melt phase after acetaldehyde removal to less than eight to 10 minutes.

The preferred practice of this invention includes:

1) melt phase polymerization; 2) melt phase devolatilization and 3) forming the polyester into shaped articles directly from the melt phase. For the purpose of illustrating the feasible methods of practice, options for polymerization, devolatilization and molding/shaping will be given.

The polymerization is preferably carried out in combination with a polymer filtration step. This filtration should be completed as early in the process as is feasible to take advantage of the lower viscosity while keeping black specks in the polymer at an acceptable level. For example, if two polycondensation reactors are used, it is preferable to place the filters between them in order to filter at a lower melt viscosity.

Two embodiments of the polymerization portion are:

- a) Conventional, high-IhV (>0.68) melt-phase reactors followed by filtration. These reactors may be those known in the art, such as disclosed in U.S. 5,055,273 or U.S. 5,207,991 which are incorporated herein by reference.
- b) Conventional melt-phase reactors making polyester of $IhV=0.4-0.65$ by any of known processes, followed by polymer filtration, followed by another device capable of continuing polycondensation to produce high-viscosity polyesters of $IhV >0.68$ and

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generating large amounts of liquid surface area. This can be accomplished by using known types of reactors and devices such as vented single-screw or twin-screw extruders (e.g.,
5 U.S. 4,107,787), thin-film evaporators (U.S. 3,678,983), thin falling strands (U.S. 3,161,710), thin films (U.S. 4,647,650), having agitators with wire-screens (U.S. 3,526,484), or having agitators made of
10 foraminous cages (U.S. 3,279,895), all of which are incorporated herein by reference.

The possible embodiments of the devolatilization & molding functions are:

- 15 a) devolatilizing the entire polymer stream in one device followed by distributing the polymer to multiple multi-cavity molding machines.
- b) distributing the polymer to a plurality of devolatilization devices each of which sends the low-acetaldehyde polymer directly to its associated
20 multi-cavity molding machine.
- c) distributing the polymer to a plurality of devolatilization devices and then distributing the devolatilized polymer from each devolatilizer to two or more molding machines.

25 The devolatilization device can be any apparatus known in the art for generating a large amount of surface area per unit volume and/or for rapidly regenerating the exposed melt surface. The devolatilization device should subject the liquid
30 surface to a low partial pressure of acetaldehyde either by inert gas purging or applied vacuum. The devolatilization apparatus may be a vented single-screw extruder (U.S. 4,107,787), a vented twin-screw extruder (U.S. 3,619,145), a rotating disk processor
35 (U.S. 4,362,852), or device which generates thin strands

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of polymer (U.S. 3,044,993), all of which are incorporated herein by reference.

In the case of a high performance final polymerization reactor, a combination of equipment design, production rates, and operating conditions can facilitate increasing the molecular weight of the polyester and devolatilizing acetaldehyde in the same piece of equipment. In this advantageous embodiment, the polymer is rapidly distributed to a plurality of multi-cavity molding machines via a gear pump linked directly to the exit of the reactor. In this embodiment, particular care must be taken to minimize the hold-up of polymer at the reactor exit and in the distribution lines going to the molding machines.

Suitable melt processing temperatures for poly(ethylene terephthalate) polymers will generally be in the range of 260 to 310°C. Of course, processing temperatures may be adjusted for other types of polyesters depending on the melting point, IhV value and the like.

The advantages of our melt to mold process are as follows:

1. Much cheaper to operate than making pellets, solid stating, drying, and remelting.
2. Energy savings
3. Parisons or molded objects have better clarity, color, no unmelts or other defects, lower concentrations of undesirable byproducts.
4. Achieves low concentrations of acetaldehyde without using additives.
5. Provides polymer melt with lower rate of acetaldehyde regeneration than that achieved with remelted pellets.
6. Lower capital requirements.

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Polymers that are particularly useful in this process include poly(ethylene terephthalate), poly(ethylene naphthalenedicarboxylate), and copolyesters containing up to 50 mole% of modifying
5 dibasic acids and/or glycols. Modifying dibasic acids may contain from 2 to 40 carbon atoms and include isophthalic, adipic, glutaric, azelaic, sebacic, fumaric, dimer, *cis*- or *trans*-1,4-cyclohexanedicarboxylic, the various isomers of
10 naphthalenedicarboxylic acids and the like. More preferably the polyesters of the present invention contain at least 80 mole% terephthalic acid, naphthalenedicarboxylic acid or a mixture thereof.

Highly useful naphthalene dicarboxylic acids
15 include the 2,6-, 1,4-, 1,5-, or 2,7- isomers but the 1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 2,3-, 2,4-, 2,5-, and/or 2,8- isomers may also be used. The dibasic acids may be used in acid form or as their esters such as the dimethyl esters for example.

20 Typical modifying glycols may contain from 3 to 10 carbon atoms and include propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and the like. The 1,4-cyclohexanedimethanol may be in
25 the *cis* or the *trans* form or as *cis/trans* mixtures. More preferably the polyesters of the present invention comprise at least 80 mole % ethylene glycol.

Particularly preferred polyesters comprise terephthalic acid and a mixture of 60 to 99 mole %
30 ethylene glycol and 40 to 1 mole % cyclohexanedimethanol.

Generally the polyesters produced in the first step of the present invention have *IhV*'s which are at least 0.5 dl/g, more preferably at least 0.65 dl/g and most
35 preferably between 0.65 and 0.85 dl/g.

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The polyesters of this invention are readily prepared using polycondensation reaction conditions well known in the art. Typical polyesterification catalysts which may be used include titanium alkoxides, dibutyl tin dilaurate, and antimony oxide or antimony triacetate, used separately or in combination, optionally with zinc, manganese, or magnesium acetates or benzoates and/or other such catalyst materials as are well known to those skilled in the art. Phosphorus and cobalt compounds may also optionally be present. Although we prefer to use continuous polycondensation reactors, batch reactors operated in series may also be used.

Although we prefer to use the polyesters in this process in an unmodified form, other components such as nucleating agents, branching agents, colorants, pigments, fillers, antioxidants, ultraviolet light and heat stabilizers, impact modifiers and the like may be used if desired.

EXAMPLES

The following examples further illustrate the invention. However it will be understood that they are provided merely for illustrative purposes, and are not intended to limit the scope of the invention in any way.

Residual acetaldehyde refers to the acetaldehyde trapped within the PET polymer matrix after some previous melt history. Residual acetaldehyde was measured by storing the sample in a freezer at -40°C until ready to analyze. At that time the sample was removed from the freezer and placed in liquid nitrogen and cryogenically ground with a small laboratory scale Wiley mill to less than 20 mesh particles. Approximately 50 grams of ground sample was loaded into a metal GC desorption tube for AA analysis. Duplicates

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were run on each sample and results averaged. The sample tubes were stored in a freezer at -40°C until GC analysis.

5 The GC desorption condition for the analysis was 10 minutes at 150°C during which time the AA is desorbed and swept into a trap and collected at liquid nitrogen temperatures by the aid of an inert carrier gas. The AA was subsequently desorbed from the trap onto a GC column and quantified by heating the cold trap to 300°C.

10 Comparison of the present results with those of 24 hour acetaldehyde desorption into a bottle headspace indicate that 1 microgram per liter of headspace AA in a 2-liter bottle is comparable to ~3 ppm of residual AA as measured in the above test.

15

EXAMPLE 1

Filtered polyethylene terephthalate (PET) modified with 3.5 mol % 1,4-cyclohexanedimethanol (a 30/70 mol% *cis,trans* - mixture) and with an IhV = 0.64 is fed to
20 vented twin-screw reactor. After a residence time of 25 min at a temperature of 275°C and a pressure of 0.75 torr, the polymer has an IhV = 0.75 and residual acetaldehyde of 5 ppm. The polymer is then pumped to
25 four separate molding machines through a system of distribution pipes & valves having a mean residence time of approximately 2 min. The molding machines each have a residence time before the polymer has been cooled below 200°C of approximately 40 sec. The amount of residual acetaldehyde in the molded 0.75 IhV preforms is
30 9 ppm.

EXAMPLE 2

PET is prepared to an IhV = 0.74 with a final melt temperature of 285°C, filtered, and then the flow is
35 split and distributed to four devolatilizing vented

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extruders. Each stream has a flow rate equal to the capacity of one multi-cavity molding machine. The polymer entering the devolatilizing extruders contains 210 ppm residual acetaldehyde. The devolatilizers are purged with nitrogen. While in the devolatilizer for a mean residence time of 15 min, the polymer is cooled to 280°C. The polymer exiting the devolatilizer has 5 ppm residual acetaldehyde, and is ejected directly to a multi-cavity molding machine. The preforms produced have an IhV = 0.77 and acetaldehyde = 8 ppm.

EXAMPLE 3

This example uses the same equipment configuration as example 2. PET is prepared to an IhV = 0.67 at 270°C in the melt-phase reactors, and it contains 60 ppm residual acetaldehyde after filtration and transport to the devolatilizing extruders. After 10 min residence time in each devolatilizer under nitrogen purge, the polymer is molded into preforms with an IhV = 0.70 and a residual acetaldehyde of 3.5 ppm.

EXAMPLE 4

This example uses the same equipment configuration as example 2. PET is prepared to an IhV = 0.75 at 270°C in the melt-phase reactors, and it contains 80 ppm residual acetaldehyde after filtration and transport to the devolatilizing extruders. After 5 min residence time in each devolatilizer under nitrogen purge, and approximately 2 min traveling to the molds before being cooled, the polymer has an IhV = 0.75 and a residual acetaldehyde content of 10 ppm. The acetaldehyde regeneration rate during the transport of the polymer out of the devolatilizer & through the molding machine to the molds is measured to be 1 ppm per minute.

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EXAMPLE 5

PET is prepared to an IhV = 0.71 at a temperature of 275°C, and is pumped through a filter and to a devolatilizer\reactor operating at 275°C and at 0.75
5 torr pressure. After a residence time of 10 minutes where residual acetaldehyde is reduced to 6 ppm, a gear pump is used to pump the polymer through a distribution system to four multi-cavity molding machines. The
10 resulting preforms have an IhV = 0.75 and a residual acetaldehyde of 10 ppm.

EXAMPLE 6

PET is prepared to an IhV = 0.5 at 275°C, and pumped through filters to another polycondensation
15 reactor operating at 275°C and 0.75 torr. This reactor generates a large amount of surface area and the polymer achieves an IhV = 0.75 in 30 min. The molten polymer with 20 ppm acetaldehyde is then pumped through a multi-hole die to generate thin threads which fall through an
20 open vessel purged with inert gas. The molten polymer is then collected at the bottom of the vessel and distributed to four molding machines. The resulting preforms have an IhV = 0.75 and a residual acetaldehyde of 10 ppm.

25

EXAMPLE 7

PET is prepared to an IhV = 0.64 by conventional technology with a final melt temperature of 285°C. After being pumped through a filter and distribution
30 system, the polymer containing 100 ppm residual acetaldehyde is fed to two devolatilizing reactors. These reactor\devolatilizers operate at 0.75 torr pressure and cool the polymer to 275°C. After a residence time of 20 min, the polymer from each
35 devolatilizer is pumped via a gear pump to two

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multi-cavity molding machines. An accumulation cavity for each molding machine is filled sequentially via an appropriate switching valve and distribution lines. In this manner steady flow from the devolatilizer\extruder is maintained. The resulting preforms have an IhV = 0.75 and a residual acetaldehyde content of 9 ppm.

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CLAIMS

1. A process for producing molded articles comprising the steps of:

- 5 a) melt reacting at least one glycol and at least one dicarboxylic acid to form a polyester having an IhV of at least 0.5 dl/g, wherein said at least one glycol is selected from the group consisting of glycols having up to 10 carbon atoms and mixtures thereof and said
10 dicarboxylic is selected from the group consisting of alkyl dicarboxylic acids having 2 to 16 carbon atoms, aryl dicarboxylic acids having 8 to 16 carbon atoms and mixtures thereof; and
- 15 b) forming said polyester into shaped articles directly from step a.
2. The process of claim 1 further comprising the step of devolatilizing said polyester to remove acetaldehyde prior to said forming step (b).
- 20 3. The process of claim 1 wherein said polyester from step a has an IhV of at least 0.65 dl/g.
4. The process according to claim 1 wherein said dicarboxylic acid comprises at least 80% mole terephthalic acid or naphthalenedicarboxylic acid.
- 25 5. The process of claim 1 wherein said glycol comprises at least 80 mole% ethylene glycol.
6. The process of claim 1 or 4 wherein said glycol is a mixture of ethylene glycol and cyclohexanedimethanol.
- 30 7. The process of claim 2 wherein reacting and devolatilizing steps are conducted in a single piece of equipment.
8. The process of claim 2 wherein said devolatilizing step is conducted via a devolatilization
35 apparatus capable of generating a large amount of

- 20 -

surface area per unit volume and/or rapidly regenerating the exposed melt surface.

5 9. The process of claim 1 wherein step b) is accomplished in one or more multi-cavity injection molding machine.

10 10. The process of claim 1 wherein step a) is conducted in an apparatus selected from the group consisting of vented single-screw extruders, twin-screw extruders, thin-film evaporators, thin falling strands and thin films having agitators made of foraminous cages.

15 11. The process of claim 2 wherein said devolatilizing is accomplished by a method selected from devolatilizing the entire polymer stream in one device followed by distributing the polymer to multiple multi-cavity molding machines;

20 distributing said polyester to a plurality of devolatilization devices each of which feeds a low-acetaldehyde polyester directly to a multi-cavity molding machine; and

25 distributing the polyester to a plurality of devolatilization devices to form a devolatilized polyester and distributing the devolatilized polyester from each of said devolatilization devices to two or more molding machines.

12. The process of claim 1 or 2 wherein said polyester has an acetaldehyde content of less than 10 ppm.

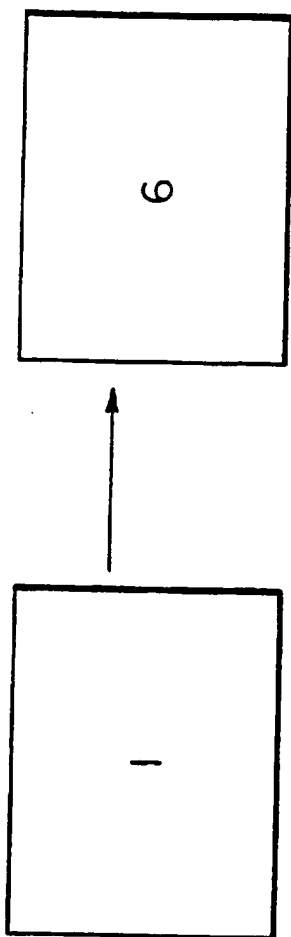


Fig. 1

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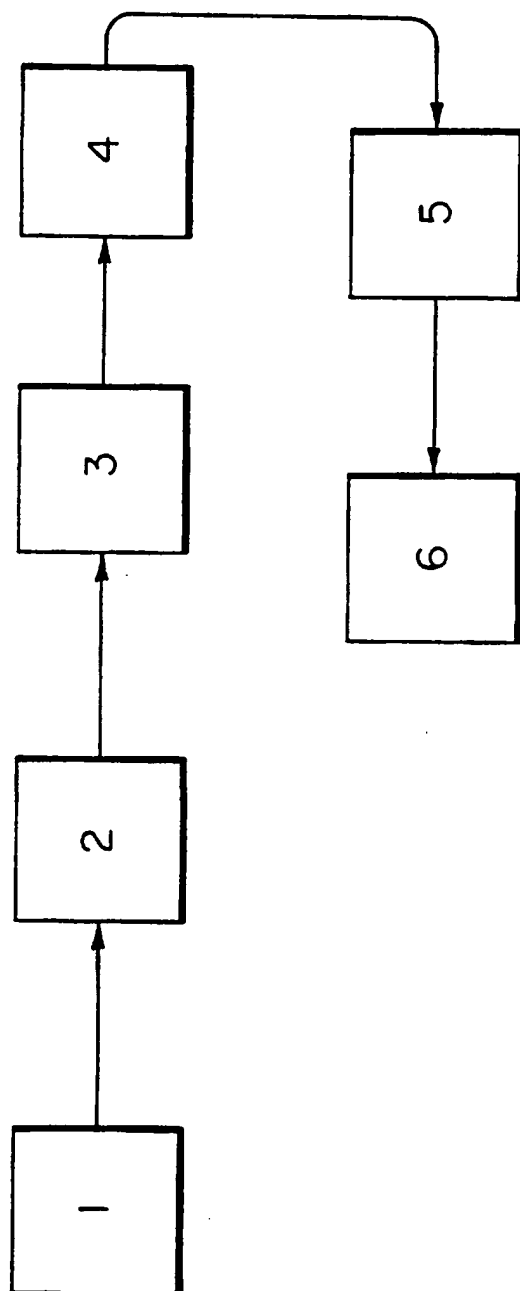


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/03037

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	INDUSTRIAL AND ENGINEERING CHEMISTRY, INDUSTRIAL SECTION, vol. 62, no. 3, March 1970, WASHINGTON US, pages 13-15, XP002032406 HEIMO HARDING-HARDING: "Continuous process for manufacture of polyester tire yarn" see page 13, right-hand column, line 1 - page 14, left-hand column, line 33; figure 1 ---	1,3
X	US 4 675 378 A (GIBBON ET AL.) 23 June 1987 see claims 1,2,12,13; figure 1 --- -/--	1,3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- *A* document member of the same patent family

Date of the actual completion of the international search

5 June 1997

Date of mailing of the international search report

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Decocker, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/03037

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 096 568 A (EASTMAN KODAK COMPANY) 18 February 1972 see claims 1-8 -----	1,3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/03037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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FR 2096568 A	18-02-72	DE 2132074 A	05-01-72
		GB 1344175 A	16-01-74
		US 3654231 A	04-04-72